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Frequency spectra of two-band fluids and fluid mixtures: Mean spherical approximation and beyond

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In the framework of a recently proposed approximation, we investigate here the frequency spectra of two-band fluids (fluids composed of particles with two independent Drude oscillators embedded) as well as fluid mixtures of particles with one Drude oscillator. Both cases are analyzed in the low density regime where departures from the linear theories are more evident. Our theory, which goes beyond the mean spherical approximation (MSA), reproduces the correct low density spectra while retaining the proper qualitative behavior of the MSA at fluid densities. © *1995 American Institute of Physics.*

I. INTRODUCTION

The problem of frequency spectra (or electronic density of states) in disordered systems has been a topic of renewed interest in recent years.[1,2] The most successful approaches to date are based on the mapping of quantum degrees of freedom into complex quantities of a model classical fluid. Two different formulations were proposed by Xu and Stratt[3] and Logan and Winn[4] that led to closely related approximations, of which the simplest approach was based on the mean spherical approximation (MSA) which is linear. In the language of Winn and Logan this was known as single superchain/effective medium approximation (SSCA/EMA). In order to overcome the low density deficiencies that stem from the linear nature of these approximations, Chen and Stratt resorted to the EXP approximation[5] and Winn and Kahl[6] extended the Logan–Winn formalism to include nonlinear effects. On a different footing two of the authors applied the Høye–Stell treatment of the quantum polarizable fluid[7] to the fluid of quantum harmonic oscillators,[8] improving upon the MSA results by perturbing the MSA on the basis of γ ordering. This approach has shown to be relatively simple with respect to numerical evaluation and to reproduce the correct low density behavior whereas retaining the nice features of the MSA at higher densities. This has been confirmed both analytically[8] and by comparison with computer simulation.[9] A natural extension of this work would then be the inclusion of several internal degrees of freedom (i.e., oscillators), which in its simplest case constitutes the two-band model (a hard-sphere fluid with two Drude oscillators embedded). This problem has already been considered both by means of the SSCA/EMA[4] and computer simulation.[10] We will in this paper see that the extension of the work by Høye and Lomba to the two-band model is relatively straightforward and leads to results in agreement with those of Refs. 4 and 10. Numerically we then restrict ourselves to the situation where the strengths of cross interactions follow the product rule.

In close relation with the two-band model, it is also relevant to study the problem of mixtures. Here, we will consider a bicomponent mixture of equal-size hard spheres with embedded Drude oscillators where each species has a different resonance frequency. Again numerically we restrict ourselves to the product rule for cross interactions. This system we study both by computer simulation (direct diagonalization of the Hamiltonian and averaging over a large collection of fluid configurations) and theoretical approximations (MSA and MSA perturbed with higher γ-ordering corrections). To our knowledge the problem of frequency spectra in mixtures has not been dealt with so far. Later we plan to come back to the more complex situation where the product rule is not fulfilled and we note in passing that the analysis for asymmetric mixtures (unequal diameters) clearly is even more involved, and will also be the subject of forthcoming work.

The rest of the paper can be sketched as follows. In Sec. II we present the theoretical analysis of the multiband model including both MSA and low density corrections. Section III is devoted the treatment of mixtures. Details of the computer simulation procedure and analysis of the results are presented in Sec. IV.

II. THEORETICAL TREATMENT OF THE MULTIBAND MODEL

As mentioned before, the two-band model can be represented by a system of hard spheres with two independent Drude oscillators, i.e., with two internal degrees of freedom. Here, we will sketch how the equations for a single oscillator per particle generalize to the situation with several oscillators in each particle. Generally, we find that scalar quantities will change into matrices, and we will here establish the relevant equations.

Between each pair of oscillators, there is a pair interaction of the form

$$\phi_{s_t s_j}(r) = s_i s_j \phi_{ij}(r) \tag{2.1}$$

with

$$-\phi_{ij}(r) = v_{ij}(r) = K_{1_{ij}} \exp[-z(r-d)]/r, \tag{2.2}$$

where $d=1$ is the hard sphere diameter, K_1 is the interaction strength and r is the interparticle spatial separation. In what

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follows, equations of Refs. 8 and 9 will be preceded by the numerals I and II, respectively, when referring to them. Equation (I2.14) becomes here

$$R_{Kij}=\int \rho_{0s}s_i s_j\, dV; \quad dV=\prod_i ds_i,$$

$$c_{Kij}(0)=v_{ij}(0)-\mathscr{C}_{ij}(0), \tag{2.3}$$

where s_i represents the coordinate of oscillator i and ρ_{0s} is the full density distribution for the oscillators. Further $\mathscr{C}_{ij}(r)$ is the so-called chain bond, and $c_{Kij}(r)$ is the direct correlation function. The second equation is valid for the MSA where the $\mathscr{C}_{ij}(r)$ becomes the correlation function itself (apart from an $s_i s_j$ factor). Equation (I2.11) becomes

$$\rho_s=B\,\exp\left(-\frac{1}{2}\sum_{ij} s_i a_{ij} s_j\right),$$

$$a_{ij}=a_{0i}\delta_{ij}-[\mathscr{C}_{ij}(0)-v_{ij}(0)], \tag{2.4}$$

$$a_{0i}=\sigma_i(K^2+\hbar^2\omega_{0i}^2), \quad \sigma_i=\frac{M_i}{\hbar^2},$$

where M_i and ω_{0i} are the reduced mass and the eigenfrequency of oscillator i, ρ_s is the density distribution of single particles that have not formed pairs in the chemical reaction picture, and B is a normalization constant Before the pair interaction is turned on, these oscillators are regarded as independent. Eq. (I2.13) becomes

$$\beta U_K=\frac{1}{2}\,(\mathrm{Tr}(\mathbf{R_K c_K}(0))-\rho^2 D_K), \tag{2.5}$$

where Tr denotes the trace operation. Equation (I2.15) for $\rho^2 D_K$ stays unchanged as given by Eq. (2.26) below except that v is changed into

$$v=s_{1i}\mathscr{C}_{ij}(r)s_{2j}. \tag{2.6}$$

In the equation above and in what follows summation over repeated indices is implicit, i.e., $a_{ik}b_{kj}=\Sigma_k a_{ik}b_{kj}$. In the general case D_k will now become much more complex to evaluate, but still feasible, since the equations will remain formally the same but with various scalar quantities transformed into matrices. For the case where $\mathscr{C}_{ij}(r)$ fulfills the product rule for cross interactions

$$\mathscr{C}_{ij}(r)=\epsilon_i\epsilon_j\mathscr{C}(r) \tag{2.7}$$

the result again becomes simple as will be shown below. Equation (I2.18) should now be replaced by

$$\mathrm{Tr}(\mathbf{aR_K})=\int \rho_s a_{ij}s_i s_j\, ds+\int \rho_{s1}\rho_{s2}a_{ij}s_{1i}s_{2j} \times\left[\frac{e^v}{G(r)}-\frac{1}{2}v^2-v-1\right]d\mathbf{s}_1\, d\mathbf{s}_2\, d\mathbf{r} \tag{2.8}$$

with ρ_s given by Eq. (2.4). We then have

$$\int \rho_s s_i s_j\, ds=\rho(\mathbf{a}^{-1})_{ij}. \tag{2.9}$$

In the last integral of Eq. (2.8) partial integration can be used noting that

$$a_{ij}s_{1j}\rho_{s_1}=-\frac{\partial\rho_{s_1}}{\partial s_{1i}} \tag{2.10}$$

by which Eq. (I2.19) is replaced by

$$\mathrm{Tr}(\mathbf{aR_K})=\rho_0\ \mathrm{Tr}(\mathbf{I})+\rho^2 D_K. \tag{2.11}$$

The $\mathbf{I}$ is the unit matrix such that $n=\mathrm{Tr}(\mathbf{I})$ is the number of oscillators ($a_{ij}(\mathbf{a}^{-1})_{ij}=\mathrm{Tr}(\mathbf{aa^{-1}})=\mathrm{Tr}(\mathbf{I})$). The ρ_0 appears in Eq. (2.11) instead of ρ due to the term in addition to D_K that results from the partial integration. This leads to the equation of chemical equilibrium (I2.20) that relates ρ and ρ_0. Equations (I2.21)–(I2.23) now become

$$\beta U^R=\frac{1}{2}\sum_K\sum_i\,(\rho_0-\sigma_i(K^2-\hbar^2\omega_{oi}^2)R_{Kii}),$$

$$\beta U^E=\beta\sum_K U_K=\frac{1}{2}\sum_k\,(\mathrm{Tr}(\mathbf{R_K c_k}(\mathbf{0}))-\rho^2 D_K),$$

$$\begin{aligned}\beta U&=\beta(U^R+U^E)\\&=\sum_K\left[\frac{1}{2}\,(\rho_0\ \mathrm{Tr}(\mathbf{I})+\mathrm{Tr}(\mathbf{aR_K})-\rho^2 D_K)\right.\\&\quad\left.-K^2\ \mathrm{Tr}(\boldsymbol{\sigma}\mathbf{R_K})\right],\\&=\sum_K\,[\rho_0\ \mathrm{Tr}(\mathbf{I})-K^2\ \mathrm{Tr}(\boldsymbol{\sigma}\mathbf{R_K})]\end{aligned} \tag{2.12}$$

using Eqs. (2.3)–(2.5) and (2.11) ($\Sigma_i=\Sigma_i\delta_{ii}=\mathrm{Tr}(\mathbf{I})$). The $K=2\pi n/\beta$ with n integer. Here, we have defined the matrix $\boldsymbol{\sigma}$ with elements

$$\sigma_{ij}=\sigma_i\delta_{ij}. \tag{2.13}$$

(The sum over i that forms the expression for βU^R is the sum over the oscillators present in each particle.)

Expression (2.12) for the resulting internal energy U determines the frequency spectrum, and similarly to Eq. (I2.25), it is now given by

$$g(m^2)=-\frac{1}{\pi\rho_0}\,\mathrm{Im}\{\mathrm{Tr}(\boldsymbol{\sigma}\mathbf{R_K})\} \tag{2.14}$$

with $m=\hbar\omega$ and where one puts $K^2=-m^2+i\gamma$ ($\gamma\to 0+$). The normalization (I2.27) will change into

$$f(0)=\int g(m^2)dm^2=\mathrm{Tr}(\mathbf{I}). \tag{2.15}$$

However, we still do not have an expression for the elements R_{Kij} that go beyond the MSA case that follows from Eqs. (2.3) and (2.4) with $\rho_{0s}=\rho_s$. That is, we need $\mathrm{Tr}(\boldsymbol{\sigma}\mathbf{R_K})$ in Eq. (2.14), which is different from the $\mathrm{Tr}(\mathbf{aR_K})$ in Eq. (2.11) used to obtain Eq. (2.12).

Like Eq. (I2.18) we now will have

$$R_{Kij}=\int \rho_s s_i s_j\, ds+\int \rho_{s_1}\rho_{s_2}\mathbf{s}_{1i}\mathbf{s}_{1j} \times\left[\frac{e^v}{G(r)}-\frac{1}{2}v^2-v-1\right]d\mathbf{s}_1\, d\mathbf{s}_2\, d\mathbf{r}. \tag{2.16}$$

Like Eq. (I2.18), Eq. (2.16) can also be partially integrated. We then again utilize Eq. (2.10) as was used to obtain Eq. (2.11). Multiplying Eq. (2.16) with a_{ij} and summing over index j we find

$$(\mathbf{aR_K})_{li}=(\mathbf{R_K a})_{il}=\rho_0\delta_{il}+\int \rho_{s_1}\rho_{s_2} \times\left[\frac{e^v}{G(r)}-v-1\right]s_{1i}\mathscr{C}_{lj}s_{2j}\, d\mathbf{s}_1\, d\mathbf{s}_2\, d\mathbf{r} \quad (2.17)$$

which specifies the elements of the matrix whose trace is found in Eq. (2.11). From this $\mathrm{Tr}(\boldsymbol{\sigma}\mathbf{R_K})$ can be obtained as

$$\mathrm{Tr}(\boldsymbol{\sigma}\mathbf{R_K})=\mathrm{Tr}[(\boldsymbol{\sigma}\mathbf{a}^{-1})(\mathbf{aR_K})]. \quad (2.18)$$

In the general case the evaluation of expression (2.18) via Eq. (2.17) will be cumbersome. However, with $\mathscr{C}_{li}(r)$ of form (2.7) and the interaction of the same form, i.e., $v_{ij}(r)=\epsilon_i\epsilon_j v(r)$ or equivalently $K_{1ij}=\epsilon_i\epsilon_j K_1$, fulfilling the product rule, Eq. (2.18) like other equations simplify considerably, and the solution can be related to the single oscillator case. We first consider the MSA for this situation. From Eqs. (2.3) and (2.4) we have then

$$R_{K_{ij}}=\rho(\mathbf{a}^{-\mathbf{1}})_{ij}. \quad (2.19)$$

To obtain the single oscillator MSA solution one must solve the Ornstein–Zernike (OZ) equation (II2.10) subject to the MSA closure (II2.11). In this equation the usual ρ factor is replaced with R_K which in the present case becomes

$$R_K=\epsilon_i R_{K_{ij}}\epsilon_j. \quad (2.20)$$

For the matrix $\mathbf{a}$ of Eq. (2.4) we now will have

$$a_{ij}=a_{0i}\delta_{ij}+c\epsilon_i\epsilon_j, \quad (2.21)$$

where $c=c_K(0)$ is again to be obtained from the single oscillator solution. The inverse can be easily computed by first guessing its appropriate form, and we find

$$(\mathbf{a}^{-\mathbf{1}})_{ij}=\frac{1}{a_{0i}}\,\delta_{ij}-\frac{c}{1+c/a_0}\,\frac{\epsilon_i\epsilon_j}{a_{0i}a_{0j}}, \quad (2.22)$$

where

$$\frac{1}{a_0}=\sum_i\ \frac{\epsilon_i^2}{a_{0i}}. \quad (2.23)$$

Thus with this inserted in Eqs. (2.19) and (2.20) we find

$$R_K/\rho=\frac{1}{a_0}-\frac{c}{1+c/a_0}\left(\frac{1}{a_0}\right)^2=\frac{1}{a_0+c}. \quad (2.24)$$

One notes that this is precisely the same relation between R_K and c as in the single oscillator case, but now with a_0 given by Eq. (2.23). Furthermore, we get

$$\mathrm{Tr}(\boldsymbol{\sigma}\mathbf{R_K}/\rho)=\sum_i\ \frac{\sigma_i}{a_{0i}}-\frac{c}{1+c/a_0}\sum_i\ \frac{\sigma_i\epsilon_i^2}{a_{0i}^2}. \quad (2.25)$$

This is used in Eq. (2.14) to obtain the frequency spectrum

To find the correction beyond MSA we start with the evaluation of the D_K term of Eqs. (2.5) and (2.11)

$$\rho^2 D_K=\int \rho_{s1}\rho_{s2}\left[\frac{e^v}{G(r)}-v-1\right]v\, d\mathbf{s}_1\, d\mathbf{s}_2\, d\mathbf{r}, \quad (2.26)$$

where by use of Eq. (I2.16) $G(r)$ is

$$G(r)=\frac{\int\rho_{s_1}\rho_{s_2}e^v\, d\mathbf{s}_1\, d\mathbf{s}_2}{\int\rho_{s_1}\rho_{s_2}\, d\mathbf{s}_1\, d\mathbf{s}_2} \quad (2.27)$$

with v given by Eqs. (2.6) and (2.7) and ρ_s given by Eq. (2.4). The integral in the denominator of Eq. (2.27) will be $((\det(\mathbf{a}))^2)^{-1/2}=\det(\mathbf{a})^{-1}$. In the numerator the v couples the $\mathbf{s_1}$ and $\mathbf{s_2}$, and we will need the determinant of a larger matrix. In order to simplify this, the matrix

$$b_{ij}=\epsilon_i\epsilon_j \quad (2.28)$$

that enters v can be diagonalized by a transformation

$$\hat{\mathbf{b}}=\mathbf{c}^{-\mathbf{1}}\mathbf{bc} \quad (2.29)$$

with

$$c_{i1}=(\mathbf{c}^{-\mathbf{1}})_{1i}=\frac{\epsilon_i}{\epsilon},$$

$$\epsilon^2=\sum_i\ \epsilon_i^2$$

by which

$$\hat{b}_{11}=\epsilon^2 \quad (2.30)$$

while $\hat{b}_{ii}=0$ $(i\neq 1)$ due to form (2.28). Thus $\hat{b}_{11}$ is the only nonzero element of $\hat{\mathbf{b}}$. Likewise we will have

$$\hat{\mathbf{a}}=\mathbf{c}^{-\mathbf{1}}\mathbf{ac},$$

$$\hat{\mathbf{a}}^{-1}=\mathbf{c}^{-\mathbf{1}}\mathbf{a}^{-\mathbf{1}}\mathbf{c} \quad (2.31)$$

with

$$(\hat{\mathbf{a}}^{-1})_{11}=\frac{1}{\epsilon^2}\,\epsilon_i(\mathbf{a}^{-1})_{ij}\epsilon_j. \quad (2.32)$$

For the determinant we now have

$$\hat{a}_{ij}\hat{A}_{lj}=\delta_{il}\,\det(\hat{\mathbf{a}})=\delta_{il}\,\det(\mathbf{a}), \quad (2.33)$$

where $\hat{A}_{ij}$ is the codeterminant. Clearly

$$\hat{A}_{lj}=(\hat{\mathbf{a}}^{-1})_{jl}. \quad (2.34)$$

The determinant that defines the numerator of Eq. (2.27) is then given by

$$(\det(\hat{\mathbf{a}}))^2-(\mathscr{C}(r)\hat{b}_{11}\hat{A}_{11})^2=(\det(\mathbf{a}))^2\left(1-\frac{\mathscr{C}^2(r)}{(a_0+c)^2}\right). \quad (2.35)$$

Where by use of Eqs. (2.22) and (2.23)

$$\epsilon_i(\mathbf{a}^{-1})_{ij}\epsilon_j=\mathrm{Tr}(\mathbf{a}^{-1}\mathbf{b})=\frac{1}{a_0}-\frac{c}{1+c/a_0}\left(\frac{1}{a_0}\right)^2=\frac{1}{a_0+c}. \quad (2.36)$$

Thus we have

$$G(r)=\left[1-\left(\frac{\mathscr{C}(r)}{a_0+c}\right)^2\right]^{-1/2}. \quad (2.37)$$

This result can be also be seen in a different way. Expanding $e^v = 1 + v + \frac{1}{2}v^2 + \cdots$ in Eq. (2.27) one obtains averages of powers of v. Since these are Gaussian averages it seems clear to us that they can be written as sums of products of $\mathrm{Tr}[(\mathbf{a}^{-1}\mathbf{b})^q]$ (q integer). With the given $\mathbf{b}$ one can further write

$$\mathrm{Tr}[(\mathbf{a}^{-1}\mathbf{b})^q] = \mathrm{Tr}[(\mathbf{a}^{-1}\mathbf{b})]^q = \left(\frac{1}{a_0 + c}\right)^q \tag{2.38}$$

by which the answer will be as with a single oscillator. For Eq. (2.26) we now find

$$\rho^2 D_K = \rho^2 (D_{1K} - D_{2K}) \tag{2.39}$$

with

$$D_{1K} = \int \left[\frac{\mathscr{C}(r)}{G(r)} \frac{d}{d\mathscr{C}(r)} G(r)\right] d\mathbf{r} = \int \frac{\mathscr{C}(r)^2}{(a_0 + c)^2 - \mathscr{C}(r)^2}\, d\mathbf{r}, \tag{2.40}$$

$$D_{2K} = \int [\mathscr{C}(r)\ \mathrm{Tr}(a^{-1}b)]^2\, d\mathbf{r} = \int \left(\frac{\mathscr{C}(r)}{a_0 + c}\right)^2 d\mathbf{r}$$

which are like expressions (I2.17).

By evaluation of $\mathrm{Tr}(\boldsymbol{\sigma}\mathbf{R}_\mathbf{K})$ the first term of Eq. (2.17) will again yield the result (2.25). With the integral of Eq. (2.17) inserted in Eq. (2.18), one by expansion must obtain terms

$$\mathrm{Tr}(\boldsymbol{\sigma}\mathbf{a}^{-1}(\mathbf{b}\mathbf{a}^{-1})^q) = \mathrm{Tr}(\mathbf{b}\mathbf{a}^{-1}\boldsymbol{\sigma}\mathbf{a}^{-1})(\mathbf{b}\mathbf{a}^{-1})^{q-1}) = \mathrm{Tr}(\mathbf{b}\mathbf{a}^{-1}\boldsymbol{\sigma}\mathbf{a}^{-1})[\mathrm{Tr}(\mathbf{b}\mathbf{a}^{-1})]^{q-1} \tag{2.41}$$

instead of the terms (2.38). That is, one factor $\mathrm{Tr}(\mathbf{b}\mathbf{a}^{-1}) = (a_0 + c)^{-1}$ in the evaluation of D_K is replaced by $\mathrm{Tr}(\mathbf{b}\mathbf{a}^{-1}\boldsymbol{\sigma}\mathbf{a}^{-1})$. From Eqs. (2.13) and (2.22) we find

$$(\boldsymbol{\sigma}\mathbf{a}^{-1})_{ij} = \frac{\sigma_i}{a_{0i}}\,\delta_{ij} - \frac{c}{1 + c/a_0}\frac{\sigma_i \epsilon_i \epsilon_j}{a_{0i} a_{0j}},$$

$$(\mathbf{a}^{-1}\boldsymbol{\sigma}\mathbf{a}^{-1})_{ij} = \frac{\sigma_i}{a_{0i}^2}\,\delta_{ij} - \frac{c}{1 + c/a_0}\left(\frac{\sigma_i}{a_{0i}^2 a_{0j}} + \frac{\sigma_j}{a_{0i} a_{0j}^2}\right)\epsilon_i \epsilon_j + \left(\frac{c}{1 + c/a_0}\right)^2 \frac{\epsilon_i \epsilon_j}{a_{0i} a_{0j}}\frac{\sigma}{a_0^2} \tag{2.42}$$

with

$$\sigma = a_0^2 \sum_i \frac{\sigma_i \epsilon_i^2}{a_{0i}^2}, \tag{2.43}$$

$$\mathrm{Tr}(\mathbf{b}\mathbf{a}^{-1}\boldsymbol{\sigma}\mathbf{a}^{-1}) = \frac{\sigma}{a_0^2}\left(1 - 2\,\frac{\frac{c}{a_0}}{1 + \frac{c}{a_0}} + \frac{\left(\frac{c}{a_0}\right)^2}{\left(1 + \frac{c}{a_0}\right)^2}\right) = \frac{\sigma}{(a_0 + c)^2}. \tag{2.44}$$

Comparing with Eq. (2.11) we now obtain

$$\mathrm{Tr}(\boldsymbol{\sigma}\mathbf{R}_\mathbf{K}) = \rho_0\ \mathrm{Tr}(\boldsymbol{\sigma}\mathbf{a}^{-1}) + \frac{\sigma}{a_0 + c}\,\rho^2 D_K \tag{2.45}$$

since here expression (2.44) replaces a factor $(a_0 + c)^{-1}$ in the evaluation of D_K as concluded above.

The first term on the right-hand side of Eq. (2.45) is expression (2.25), so with expression (2.45) for σ and Eq. (2.23) for a_0 we obtain

$$\mathrm{Tr}(\boldsymbol{\sigma}\mathbf{R}_\mathbf{K}) = \rho_0 \sum_i \frac{\sigma_i}{a_{0i}} + \frac{\sigma}{a_0 + c}\left(-\rho_0\,\frac{c}{a_0} + \rho^2 D_K\right). \tag{2.46}$$

This is to be inserted in Eq. (2.14) to obtain the frequency spectrum.

Evaluation of expression (2.20) can now be performed in the same way replacing $\boldsymbol{\sigma}$ with $\mathbf{b}$ ($b_{ij} = \epsilon_i \epsilon_j$). The factor (2.44) is then replaced by $\mathrm{Tr}(\mathbf{b}\mathbf{a}^{-1}\mathbf{b}\mathbf{a}^{-1}) = [\mathrm{Tr}(\mathbf{b}\mathbf{a}^{-1})]^2 = (a_0 + c)^{-2}$, and the MSA result (2.24) changes into

$$R_K = \rho_0\ \mathrm{Tr}(\mathbf{b}\mathbf{a}^{-1}) + \mathrm{Tr}(\mathbf{b}\mathbf{a}^{-1})\rho^2 D_K = \frac{\rho_0 + \rho^2 D_K}{a_0 + c} \tag{2.47}$$

which again is Eq. (I2.19).

Altogether we can conclude that the equations reduce to those of the single oscillator case with Eq. (2.23) inserted for a_0. In Eq. (2.45) expression (2.43) is inserted for σ. For higher densities the ρ^2 in front of D_K is again replaced by the μ factor used in Eqs. (I4.4) and (I4.6), and expressions (2.46) and (2.47) can be modified accordingly. Also the D_{1K} and D_{2K} terms can be modified into form (I6.1). The numerical work can then also be performed as before using the same methods. Equation (2.46) can be rewritten somewhat utilizing result (2.47). We obtain

$$\mathrm{Tr}(\boldsymbol{\sigma}\mathbf{R}_\mathbf{K}) = \rho_0\left(\sum_i \frac{\sigma_i}{a_{0i}} - \frac{\sigma}{a_0}\right) + \sigma R_K. \tag{2.48}$$

Thus modifications to R_K in Eq. (2.47) immediately apply to Eq. (2.48) which by insertion in Eq. (2.14) gives the frequency spectrum. These modifications are discussed in connection with Eq. (II2.23) used by numerical evaluation in the single oscillator case. Also the problem with the proper solution at low density will be identical.

Our computational scheme now needs the solution of the MSA problem, the OZ equation (II2.10) with MSA closure (II2.11), which altogether can be expressed in terms of a single parameter u_0.[11] The MSA frequency spectrum can be determined by solving Eq. (2.24) for u_0 coupled with Eqs. (II2.12)–(II2.14) and (II2.16) for given z and ρ, and sampling along the frequency axis, i.e., varying $a_{01} = \sigma_1(K^2 + \hbar^2\omega_{01}^2)$ and $a_{02} = \sigma_2(K^2 + \hbar^2\omega_{02}^2)$. This will produce the values of E/J from Eq. (II2.17) and the frequency spectrum (or energy density of states) from Eq. (2.14). Here, $E/J = a_0 e^{-z}/K_1$ where now a_0 is given by Eq. (2.23) and K_1 is the strength of interaction such that $K_{1ij} = K_1 \epsilon_i \epsilon_j$ in Eq. (2.2).

In order to implement the corrections to the MSA, we employ the same procedure as for the derivation of Eq. (II2.23), but using the a_0 value given by Eq. (2.23). With this Eq. (2.47) becomes

$$\rho/R_K = a = (a_0 + c_K(0))\,\frac{1+\mu^2 D_{2K}/\rho}{1+\mu^2 D_{1K}/\rho}. \tag{2.49}$$

We need to evaluate the chain bond appearing in Eq. (2.40). This quantity should be computed with core condition implied on $h_K(0)$,[12] but previous experience indicates that this causes numerical instabilities.[13] A reasonable approximation which we use here, is the use of the MSA chain bond, i.e., the MSA $h(r)$ for which analytic expressions are available from Eqs. (II2.19)–(II2.22)

III. FREQUENCY SPECTRA FOR MIXTURES

In this section we present the generalization of the one-component equations to binary mixtures. For simplicity we assume that only one oscillator is embedded in each particle. To denote the various components we will use subscripts i and j. Equations (I2.11)–(I2.14) now become

$$\rho_{is} = B_i \exp(-\tfrac{1}{2}a_i s^2),$$

$$a_i = a_{0i} - (\mathscr{C}_{ii}(0) - v_{ii}(0)),$$

$$a_{0i} = \sigma_i(K^2 + \hbar^2\omega_{0i}^2); \quad (\sigma_i = M_i/\hbar^2), \tag{3.1}$$

$$\beta U_K = \frac{1}{2}\left[\sum_i R_{iK}\mathscr{C}_{iiK}(0) - \sum_{ij}\rho_i\rho_j D_{ijK}\right], \tag{3.2}$$

$$R_{iK} = \int \rho_{0is}s^2\, ds,$$

$$c_{iiK}(0) = v_{ii}(0) - \mathscr{C}_{ii}(0). \tag{3.3}$$

Equations (I2.17) and (I2.19) transform into

$$D_{ij1K} = \int \frac{\mathscr{C}_{ij}^2(r)}{a_i a_j - \mathscr{C}_{ij}^2(r)}\, d\mathbf{r},$$

$$D_{ij2K} = \int \frac{\mathscr{C}_{ij}^2(r)}{a_i a_j}\, d\mathbf{r},$$

$$D_{ijK} = D_{ij1K} - D_{ij2K}, \tag{3.4}$$

$$R_{iK} = \frac{1}{a_i}\left(\rho_{0i} + \sum_j \rho_i\rho_j D_{ijK}\right), \tag{3.5}$$

and Eq. (I2.23) becomes

$$\beta U = \sum_K \sum_i (\rho_{0i} - \sigma_i K^2 R_{iK}). \tag{3.6}$$

For higher densities expression (3.5) as well as Eq. (I2.19) are modified to include the μ factor of Eq. (I4.2) which reads

$$B_4 = \mu = \frac{\partial\rho}{\partial(\beta g)}, \tag{3.7}$$

where g is the chemical potential for the reference system fluid (without oscillators embedded). From the fluctuation theorem one also has

$$\mu = \rho + \rho^2\tilde{h}(0),$$

$$\tilde{h}(0) = \int h(r)d\mathbf{r}, \tag{3.8}$$

where $h(r)$ is the pair correlation function. Likewise for mixtures we have the corresponding hypervertices

$$\mu_{ij} = \frac{\partial\rho_i}{\partial(\beta g_j)} = \rho_i\delta_{ij} + \rho_i\rho_j\tilde{h}_{ij}(0). \tag{3.9}$$

When the different species are equal except for the internal oscillators (e.g., they have the same hard sphere diameter) then they all will have the same correlation function, so we can write

$$\tilde{h}_{ij}(0) = \chi = \frac{\mu-\rho}{\rho^2}, \tag{3.10}$$

where again $\mu=\mu(\rho)$ ($\rho=\Sigma_i\rho_i$) is the one component quantity as defined by Eq. (3.7) or (I4.2) ($\mu=\rho+\rho^2\chi$).

Now consider the graph with four $\mathscr{C}$ bonds in D_{ijK}. With the μ_{ij} included for higher densities it now becomes

$$A_4 = \sum_{lk}\mu_{ik}\mu_{jl}\,\frac{\mathscr{C}_{ij}\mathscr{C}_{kj}\mathscr{C}_{kl}\mathscr{C}_{il}}{a_i a_k a_j a_l} \tag{3.11}$$

($\mathscr{C}_{ij}=\mathscr{C}_{ij}(r)$). We do not expect terms $\mathscr{C}_{ij}^2\mathscr{C}_{kl}^2$ to contribute here since they would represent induced spatial correlations which are absent in the quenched system, as discussed shortly above Eq. (I2.16).

Now consider the situation where the product rule for cross interactions is fulfilled

$$\mathscr{C}_{ij}(r) = \epsilon_i\epsilon_j\mathscr{C}(r). \tag{3.12}$$

By use of Eqs. (3.9) and (3.10) Equation (3.11) then becomes

$$A_4 = \mu_i\mu_j\left(\frac{\mathscr{C}_{ij}^2}{a_i a_j}\right)^2 \tag{3.13}$$

with

$$\mu_i = \rho_i\left(1 + \frac{a_i}{\epsilon_i^2}\chi s\right),$$

$$s = \sum_l \frac{\rho_l}{a_l}\epsilon_l^2. \tag{3.14}$$

Higher order vertices are not treated correctly anyway. Thus in view of Eq. (I4.4) and result (3.13), we now replace Eq. (3.5) with

$$R_{iK} = \frac{1}{a_i}\left(\rho_{0i} + \sum_j \mu_i\mu_j D_{ijK}\right) \tag{3.15}$$

with μ_i, χ, and D_{ijK} given by Eqs. (3.14), (3.10), and (3.4), respectively.

For the situation with $\mathscr{C}_{ij}(r)$ given by Eq. (3.12), we for a_i given by Eqs. (3.1) and (3.3) obtain

$$a_i = a_{0i} + \epsilon_i^2 c_K(0) \tag{3.16}$$

with

$$c_K(0) = v(0) - \mathscr{C}(0). \tag{3.17}$$

Similar to Eq. (II2.2) the interaction will now be ($\phi\to\phi_{ij}$)

$$-\phi_{ij}(r) = v_{ij}(r) = \epsilon_i\epsilon_j K_1 e^{-z(r-d)/r} \tag{3.18}$$

for the case with $\mathscr{C}_{ij}(r)$ given by Eq. (3.12), and with interaction of Yukawa form.

For the case considered above we can now conclude that the equations reduce to the ones of the single oscillator case. The single component OZ equation (II2.10) will then also be the one for the mixture replacing R_K with

$$R_K=\sum_i R_{iK}, \tag{3.19}$$

where R_{iK} is given by Eq. (3.15). Like Eq. (I4.6) the R_{iK} can also be modified into

$$R_{iK}=\frac{\rho_i+\Sigma_j\mu_i\mu_j D_{ij1K}}{a_i\left(1+\frac{1}{\rho_i}\Sigma_j\mu_i\mu_j D_{ij2K}\right)} \tag{3.20}$$

with $D_{ij\nu K}$ (ν=1,2) given by Eq. (3.4). Further, the $D_{ij\nu K}$ terms are modified into form (I6.1) replacing μ^2 with $\mu_i\mu_j$, $\mathscr{C}_{ij}(r)$ with $\epsilon_i\epsilon_j\mathscr{C}(r)$, and a^2 with a_ia_j. Also the pair correlation $h_0(r)$ of the reference system hard spheres enter the integrals of these expressions.[9] The numerical procedure used in connection with Eq. (II2.23) and the previous section can be applied. Note, however, that the a_i to be used in the D_{ij1K} and D_{ij2K} cannot be redefined directly in terms of $a_i=\rho_i/R_{Ki}$ due to the coupling of several a_i in Eq. (3.5) [see Eq (II2.23) and discussion in connection to it]. Therefore we first used an a_i given by $a_i^n=\rho_i/R_{Ki}^{n-1}$, where n denotes the iteration number in the iterative solution procedure. This turned out to be a source of additional computational difficulties namely slow convergence and instabilities in a small region bounded by the two resonance frequencies. The procedure to overcome this difficulties is twofold. First, numerical stability is enhanced by use of a mixing iterates procedure on the a_i terms, i.e.,

$$a_i^{i+1}=(1-\alpha)\rho_i/R_{Ki}^{i-1}+\alpha\rho_i/R_{Ki}^i, \tag{3.21}$$

where α is an adjustable parameter. In addition a further source of instability can be eliminated neglecting the D_{111K} term for $\omega\gg\omega_{01}$, i.e., when its value is sufficiently small, otherwise a wrong contribution arises from extra poles in $(1)/(a^2-\mathscr{C}^2)$ in Eq. (3.4).

As already noted in Ref. 9, problems connected with the low density singularity in the function $a=a(a_0)$ can be removed by solving Eq. (3.19) with the D_{2K} terms neglected and then the resulting a values are used in Eq. (3.19) including the D_{2K} terms.

IV. COMPUTER SIMULATION AND THEORETICAL RESULTS

Following the procedure of Gibbons *et al.*,[14] we have used a hard sphere Monte Carlo program to generate the spatial distributions of the hard sphere fluid. We have used a sample of 500 particles, and the eigenvalue evaluation and averaging were performed every 200 cycles along a 10^5 cycles run (where each cycle implies the displacement of the N particles). The total energy due to the integral degrees of freedom for the two-band model is

$$\begin{aligned}V^a(s_1^a\cdots s_N^a,s_1^b\cdots s_N^b;r_1\cdots r_N)&\\ =\frac{1}{2}\sum_i\,(M_a\omega_{0a}^2(s_i^a)^2+M_b\omega_{0b}^2(s_i^b)^2)&\\ +\sum_{i>j}\,(\phi^{aa}(r_{ij})s_i^as_j^a+\phi^{bb}(r_{ij})s_i^bs_j^b)&\\ +\sum_{i>j}\,(\phi^{ab}(r_{ij})s_i^as_j^b+\phi^{ba}(r_{ij})s_i^bs_j^a),&\end{aligned} \tag{4.1}$$

where each type of oscillator is denoted by a and b, and $s_i^a(s_i^b)$ is the coordinate of the internal degree of freedom a (or b) in particle i. With this, the normal modes are determined by solving the $2N\times 2N$ determinant

$$\left|\begin{pmatrix}M_a(\omega^2-\omega_{0a}^2)\mathbf{I} & 0\\ 0 & M_b(\omega^2-\omega_{0b}^2)\mathbf{I}\end{pmatrix}-\begin{pmatrix}\mathbf{J^{aa}} & \mathbf{J^{ab}}\\ \mathbf{J^{bb}} & \mathbf{J^{ba}}\end{pmatrix}\right|=0, \tag{4.2}$$

where $(\mathbf{J}^{\alpha\beta})_{ij}=\epsilon_\alpha\epsilon_\beta\exp(-zr_{ij})/r_{ij}$ (α, β=a,b) and $\mathbf{I}$ is a $N\times N$ unit matrix.

For a binary mixture one has

$$\begin{aligned}V^a(s_1^a\cdots s_{Na}^a,s_{Na+1}^b\cdots s_N^b;r_1\cdots r_N)&\\ =\frac{1}{2}\sum_{i\geqslant 1}^{N_a}M_a\omega_{0a}^2(s_i^a)^2+\frac{1}{2}\sum_{i>N_a}^{N}M_b\omega_{0b}^2(s_i^b)^2&\\ +\sum_{i>j\geqslant 1}^{Na}\phi^{aa}(r_{ij})s_i^as_j^a+\sum_{j\geqslant 1}^{N_a}\sum_{i>N_a}^{N}\phi^{ab}(r_{ij})s_i^as_j^b&\\ +\sum_{i>j>N_a}^{Nb}\phi^{bb}(r_{ij})s_i^bs_j^b,&\end{aligned} \tag{4.3}$$

where particles 1,2,..,N_a correspond to species a, and particles $N_{a+1,\ldots,N}$ to species b. Again the normal modes are evaluated by solution of the $N\times N$ determinant

$$\left|\begin{pmatrix}M_a(\omega^2-\omega_{0a}^2)\mathbf{I}_{N_a\times N_a} & 0\\ 0 & M_b(\omega^2-\omega_{0b}^2)\mathbf{I}_{N_b\times N_b}\end{pmatrix}-\begin{pmatrix}\mathbf{J^{aa}} & \mathbf{J^{ab}}\\ \mathbf{J^{bb}} & \mathbf{J^{ba}}\end{pmatrix}\right|=0, \tag{4.4}$$

where $(\mathbf{J}^{\alpha\beta})_{ij}=\epsilon_\alpha\epsilon_\beta\exp(-zr_{ij})/r_{ij}$ (α, β=a,b) and the subscripts $N_i\times N_i$ indicate the order of the submatrix. In both cases the problem reduces to the determination of the eigenvalues ω^2. And like Eq. (II2.17) the ω^2 are related to the energies E by $E/J=\sigma_1\hbar(\omega_{01}^2-\omega^2)e^{-z}/K_1\epsilon_1^2$.[9]

We have thus computed the density of states for two different densities and two different screening factors for the two-band model (Figs. 1–2). The binary mixture has been studied for several mol fractions and constant total density (ρd^3=0.1) and screening factor (z=0.5). The difference in the resonance frequency was set to $\sigma\hbar^2(\omega_{0b}^2-\omega_{0a}^2)/K_1=1$ ($\sigma_1=\sigma_2=\sigma$), and all coupling constants are considered identical (i.e., $\epsilon_1=\epsilon_2=1$).

Figure 1 shows the clear improvement upon the MSA results, obtained for the two-band model, both in the height of the low frequency peak as in the corrections of the tails. For the larger screening case (z=0.9) both the MSA and the perturbed MSA theory miss somewhat the position of the smooth higher frequency peak. As already shown by Bush *et al.*,[10] when the coupling constants are identical there is no band overlap, and the gap increases with higher screening

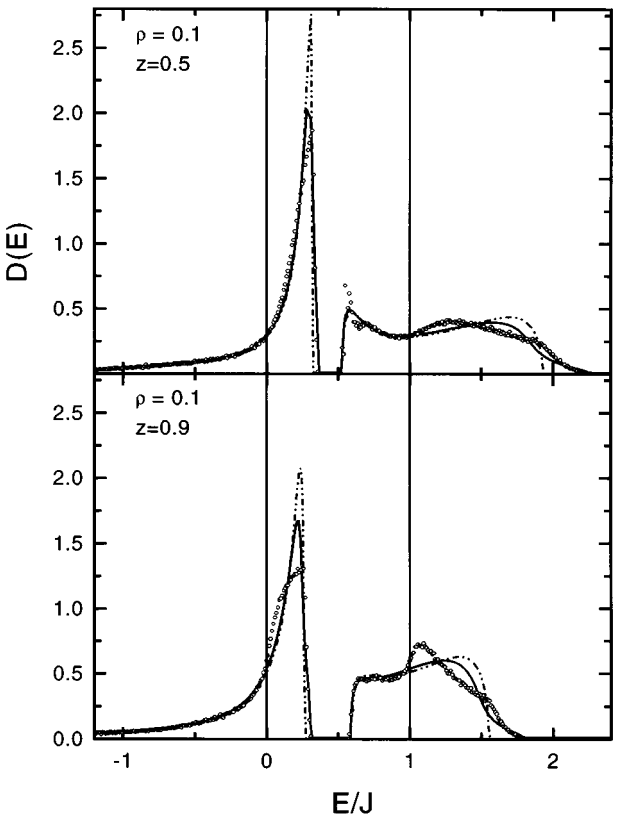

FIG. 1. Frequency spectrum for a hard sphere fluid with two embedded Drude oscillators for $\rho d^3=0.1$ and two different screening factors z in the Yukawa interaction. The difference in resonance frequency is given by $\sigma\hbar^2(\omega_{0b}^2-\omega_{0a}^2)/K_1=1$. Simulation results are denoted by open circles, a solid curve represents the perturbed MSA theory, and results from the plain MSA are denoted by a dash–dot curve.

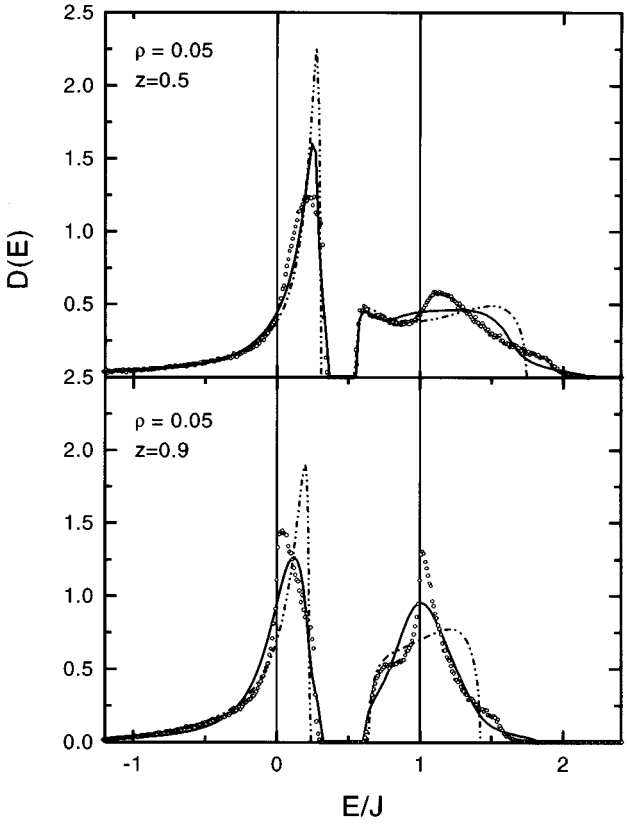

FIG. 2. Same as Fig. 1 for $\rho d^3=0.05$.

(i.e., increasing z). The presence of this band gap is a general property present when the cross interaction fulfill the product rule which implies Eq. (2.7) in our theory. This can then be deduced from Eq. (2.23) for a_0. With a_{0i} given by Eq. (2.4) it then follows that $a_0=\infty$ at some point within each interval between neighboring single oscillator eigenfrequencies. Large a_0 (or small $R_K\to 0$) and thus $a_0\to\infty$ implies a real solution and hence no eigenfrequency. This prediction of band gaps is also in accordance with our simulations. Comparing Figs. 1 and 2 (for $\rho d^3=0.1$ and $\rho d^3=0.05$, respectively) we appreciate that increase of density implies a blue shift in particular for the low frequency band, which also falls more sharply on the high frequency side. The high frequency peak is slightly blue shifted and somewhat smeared out, in contrast to the low frequency peak for which the shift is more apparent, and the latter is also sharper and more asymmetric. At both densities the improvement of the perturbed MSA theory compared with MSA itself is obvious.

In Fig. 3 we have collected the most representative results for the bimolecular mixture problem. The calculations were performed at constant density varying the mol fraction of the component with lowest resonance frequency (species a). The high frequency peak is always blue shifted, although the shift decreases as the number of particles b diminishes. We see that the spectra is not symmetric with regard to the

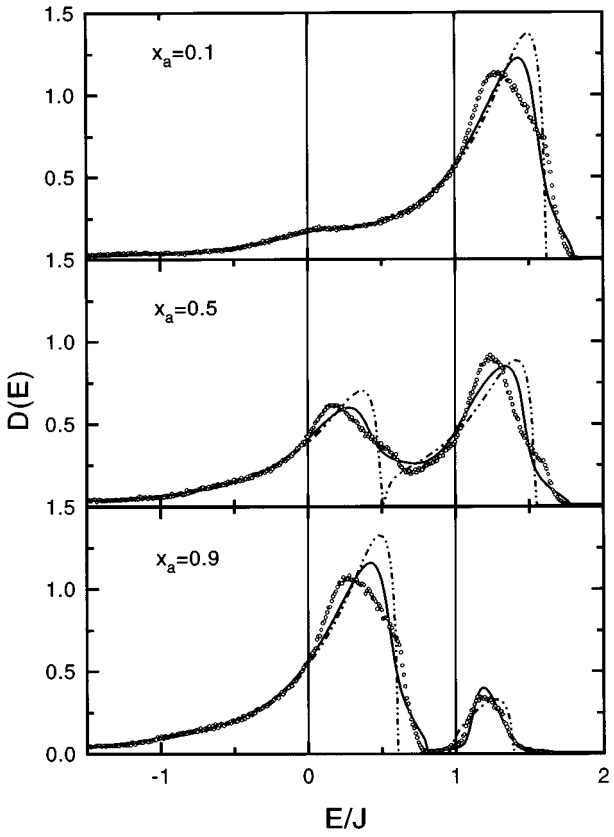

FIG. 3. Frequency spectra for a binary fluid mixture at fixed total density ($\rho d^3=0.1$) and varying mol fraction x_a. Difference in resonance frequency and symbols are as in Fig. 1. The Yukawa screening factor $z=0.5$.

number of particles of type *a* or *b*, i.e., the band corresponding to species *a* is hardly visible for small mol fractions, whereas that of species *b* is still perfectly noticeable for an equivalent low concentration. If each band were to be normalized separately (which is only possible when there is a clear band gap) the difference would be more apparent. Again here the perturbed MSA theory represents a remarkable improvement upon the plain MSA results, in particular for equimolecular compositions, where the MSA even predicts an nonexistent gap.

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